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Final Report

Development of Synthesis and Large Scale Production Technology for Ultrahigh Energy and Density Fluoro-Organic Compounds

Phase I – STTR

Contract F49620-01-C-0046

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EXECUTIVE SUMMARY

The goals of this Phase I STTR project were to address the technical feasibility and commercial aspects of producing high-density fluorine-rich compounds that are significantly more reactive and energetic than conventional explosives to neutralize and destroy chemical and biological agents. During the one-year, Phase I STTR grant to NeTech, Inc., with subcontract to the University of Florida Department of Chemistry, the broad goals of the incipient project have been accomplished:

1. Two high density, pentafluorosulfanyl (SF_5) group-containing polymers have been identified as feasible products—namely an SF_5 -containing derivative of polybutadiene and a polymer derived from SF_5 -cyclopropene.
2. A new, broadly significant synthetic methodology for introduction of the SF_5 -substituent into aliphatic compounds has been invented and can be applied to the preparation of these two products.
3. Preliminary synthetic studies have demonstrated the feasibility of preparation of both of these products.
4. The understanding of the chemistry involved indicates that scale up of the procedures should not pose a special problem.
5. The cost of preparing either of these two products on a large scale should be relatively low.
6. Initial contact with two chemical industries (Dupont and Ozark International) with expertise and interest in processing and production of fluorinated compounds has generated significant interest in pentafluorosulfanyl (SF_5) group-containing polymers.
7. Experimental facility with high-pressure combustion chamber capable of full range testing of pentafluorosulfanyl (SF_5) group-containing polymers has been identified.

INTRODUCTION

The goals of this Phase I STTR project were to address the technical feasibility and commercial aspects of producing high-density fluorine-rich compounds that are significantly more reactive and energetic than conventional explosives to neutralize and destroy chemical and biological agents. The project combined the scientific research base of the University of Florida Department of Chemistry with the technology marketing expertise of New Era Technology, Inc. (NeTech) to conduct the Phase I, R&D effort. This effort was also able to leverage results of a basic science research effort conducted under a joint ISCT project (Title: Research on Combustion of Organophosphorous Esters: Burning Velocities and Flammability Limits) at the Institute of Physiological Active Compounds (Chernogolovka, Russia) and at the Institute of Chemical Physics (Moscow Region Russia.)

The primary focus of this Phase I STTR was to evaluate high density, SF_5 -containing materials as potential non-explosive, high-energy compounds to neutralize and destroy chemical and biological agents. The SF_5 group added to certain polymers can provide energetic materials with improved properties (increased density, decreased sensitivity and good thermal stability) as well as produce energy in the combustion. For example, the Russians patented the reaction products from SF_5NF_2 and alkenes as rocket fuels. There are indications that the SF_5 group will provide compounds with increased density. For example, $\text{C}_6\text{H}_5\text{SF}_5$ has a density of 1.49, whereas $\text{C}_6\text{H}_5\text{NO}_2$ has a density of 1.20 g/mL. This Phase I investigation of the effect of the pentafluorosulfanyl group on the energetic properties of organic hydrocarbon compounds was based upon the following considerations:

1. Indications that the SF₅ group can provide compounds with improved properties, i.e., increased density, decreased sensitivity and good thermal stability;
2. Predicted energy release due to formation of HF in the detonation SF₅ energetic compounds [compare the average S-F bond energy (79 kcal/mole) to that of H-F (136 kcal/mole)];
3. Predicted energy release from SF₅ compounds in metallized compositions (for example, compare the respective S-F and Al-F bond energies, 79 and 158 kcal/mole respectively).

Motivation and Considerations for the Destruction of Biological and Nerve Agents

This development is important because of the deadly nature of the threat posed by biological and nerve agents (BANA). In considering the problem, there are several broad scenarios that have been considered to guide this effort at destruction of biological and nerve agents (DBANA). These scenarios are:

1. Releases resulting from the destruction of a bunker or depot in a hostile area with the potential for fallout to affect friendly or innocent populations.
2. Releases resulting from high altitude intercept of a warhead bearing BANA.
3. Deployment of BANA against a friendly population by an aggressor.

Each scenario offers some slightly different challenges with the last scenario being the most difficult due to the need to minimize collateral damage and not cause greater harm to a friendly population in neutralizing the BANA.

The first two scenarios are similar in nature presenting the problem of neutralizing residual BANA following the destruction of a warhead or bunker. Once storage containers or warheads (of submunitions) containing BANA are hit and broken up, the “rain down” or dispersal of the “cloud” on friendly populations must be prevented. The mechanism studied in this STTR is to consume the cloud by a secondary explosion (or

rapid reaction) of residual propellants and high-energy fluorine-containing compounds used to enhance the neutralization. A “dual-kill” approach is thus proposed to minimize cost and maximize the probability of success. First a missile is deployed to rupture a storage area or intercept a warhead at high altitude. This “bunker busting” or agile intercept missile is followed by a warhead that contains fluorine-rich, highly-energetic materials that complete the neutralization via rapid chemical reactions. It is important to note that the second energetic warhead does not require either high velocity or hit-to-kill guidance and control. This second missile is essentially a high-speed tanker of neutralizing agent with a spray system much like a remotely operated crop-duster that could be command guided to the region of BANA release. During reaction, this over-oxidized payload should yield free fluorine to provide a more energetic reaction.

For scenario one and two above, the parameters of the threat such as intercept altitude, number of warheads, etc. are defined by the theater. For example within a given theater, the type of missile and delivery system will be known. However, the configuration of a warhead carrying BANA and their composition may not be known. Thus, once the intercept or destruction has occurred and the agents are dispersed, the approach for neutralizing them must be sufficiently robust to overcome these uncertainties.

For the case of neutralization at 10 to 40 km altitude in the middle of a war, the neutralization can be violent and use agents that could not be used in a populated area. However, as mentioned earlier, scenario three is the most challenging due to the potential for collateral damage as might result from a BANA attack on office buildings, subways, etc. In these cases, people are already exposed and the neutralization has to be

compatible with minimizing casualties. Therefore, methods are desired for a controlled application of the neutralizing compound. Besides considering their overall effectiveness at neutralizing the BANA, effects from the reaction products may not be entirely benign. The secondary effects of using fluorinated neutralizing-agents must be considered as well as their potential for less than 100% destruction of the threat.

Research and development into methods to neutralize these threats is important because of the large scale and deadly nature of the threat posed by BANA. Highly energetic and reactive compounds offer an opportunity to neutralize and destroy these agents. Therefore, strong $SF_5/NO_2/NF_2$ -substituted oxidizers should be able to be deployed in the battlefield to reduce the threat posed by BANA. This Phase I research sought to investigate the synthesis and testing of SF_5 -containing compounds that should be more reactive and energetic than conventional explosives.

Phase I Experimental Research

The primary goal has been to design polymer (and sometimes precursor monomer) targets that bear as high a ratio of SF_5 to carbon as synthetically feasible, so as to maximize the density and fluorine-content of the substances.

A second important goal was to *increase the energy* of the polymer as high as possible, to enhance the combustion enthalpy of the polymer, while maintaining a low explosive character. Thus the target compounds are strained hydrocarbon compounds bearing SF_5 substituents. It should be noted that such organic compounds containing only C, H, and SF_5 could never be considered “high energy” compounds (per mole). However, they can provide high energy per unit volume.

Other important characteristics that should be characteristic of these two products is that they will be high melting solids; they will have high thermal stability ($>350\text{ }^{\circ}\text{C}$); they will have excellent air and moisture stability; and therefore they will have a long shelf life.

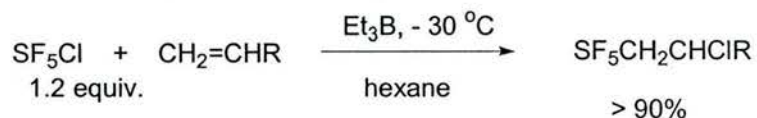
It is expected that materials with such characteristics may be able to be used as matrix materials in mixtures with certain, *true* high-energy materials such as $\text{NF}_4^+\text{BF}_4^-$ or even N_2F_4 .

EXPERIMENTAL RESULTS

1. **Inventions: Invention of new synthetic methodology for incorporation of SF_5 groups into aliphatic organic compounds.**

Post-doctoral fellow, Dr. Samia Ait-Mohand, working in the laboratory of Prof. William R. Dolbier, Jr. at the University of Florida, developed a clean and facile method for adding SF_5Cl to aliphatic alkenes or alkynes, hydrocarbon or functionalized organic compounds. In the past, the only way to put SF_5 substituents into organic compounds has been the thermally- or photochemically-induced free radical addition of SF_5Cl or, better yet, SF_5Br to alkenes. The thermal reactions had to be carried out in autoclaves, at high temperatures, for long periods, whereas the photochemical process also required specialized equipment and long reaction times. This breakthrough will make synthesis of small or large quantities of SF_5 -substituted aliphatics much easier and safer than has been the case in the past. On the basis of model compound testing, scale up of the synthesis of the two target compounds identified below should be much more easily and safely implemented.

This discovery reveals that SF₅Cl can be induced to undergo free radical chain addition to a wide variety of unsaturated organic compounds by a Et₃B-induced procedure at -30 °C, at atmospheric pressure, in 1 hour in yields greater than 90%. Thus



the reaction of SF₅Cl, using only a modest 1.2 equivalent excess, with alkenes such as 1-octene, isobutylene, cyclohexene, vinyl acetate and even α , β -unsaturated ketones and esters proceeds smoothly. This is truly a breakthrough in synthetic methodology that will provide much greater access to SF₅-containing compounds with a much wider variety of functionalities present. It will also facilitate any scale-up processes of such compounds in the future.

This new and improved method is exemplified below, and a Table of results is provided that demonstrates the excellent yields obtained when using the procedure. These results constitute a true breakthrough in methodology for putting SF₅ groups into organic compounds.

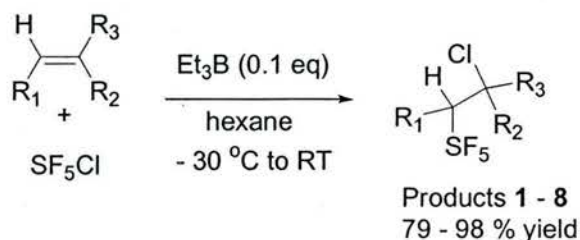
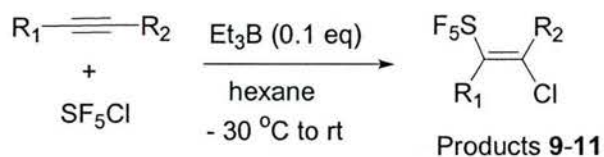


Table 1. Yields for addition of SF₅Cl to alkenes^a

R ₁	R ₂	R ₃	Product, (% yield)
H	<i>n</i> -C ₆ H ₁₃	H	1 , 95
H	<i>n</i> -C ₄ H ₉	H	2 , 98 ¹⁹
H	<i>t</i> -C ₄ H ₉	H	3 , 96
H	C ₂ H ₅	C ₂ H ₅	4 , 89
<i>n</i> -C ₃ H ₇	H	<i>n</i> -C ₃ H ₇	5 , 95 ^b
(CH ₂) ₄		H	6 , 98 ^{b, 11}
H	<i>p</i> -tolyl	H	7 , 79
H	OAc	H	8 , 98 ²⁰

^a in hexane, at – 30 °C, 0.1 equiv. Et₃B, 30 minutes^b one major diastereomer (> 90% by NMR)**Table 2.** Addition of SF₅Cl to Alkynes^a

R ₁	R ₂	Product, ^b % yield
<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	9 , 93
H	<i>n</i> -C ₆ H ₁₃	10 , 94
H	Ph	11 , 94 + 12 , 27

^a in hexane, at – 30 °C, 0.1 equiv. Et₃B, 30 minutes^b Single diastereomer in each case

The required source of SF₅ in this procedure is SF₅Cl, which is commercially available, but presently quite expensive. However, in the event that large quantities of

SF₅Cl are required, as they would be if this project moves forward, there are a number of companies that should be able to manufacture it using the ultimate raw materials F₂, S, Cl₂ and KF or CsF. Therefore, in principle SF₅Cl should not be prohibitively expensive. One Japanese company, Kanto Denka, has already indicated an interest in its manufacture, but Air Products, DuPont or possibly Ozark Fluorine Specialties would also be feasible sources in the U. S. Any of these companies (plus others) would also be potential partners for manufacture of the final polymeric product.

2. **Significant Interactions: Observations from Russian research on combustion testing and synthesis of SF₅ containing polymers.**

Cooperative efforts with the laboratories of Drs. Valery Brel and Vlad Slutsky in Moscow provided confirmation of the hypothesis that the presence of SF₅ substituents in organic compounds will serve to enhance the energetic properties of these compounds in combustion. Professor Slutsky has found that, in comparison to propene (CH₃CH=CH₂), the SF₅-substituted analog, CH₃CH=CHSF₅ provides a much more energetic reaction in combustion.



Synthesis of SF₅CH=CHCH₃ was performed by Dr. Brel and provided this model compound to Prof. Slutsky for combustion testing. Although the rate of combustion was slower, it was nevertheless very effective, and exhibited properties in lean mixtures that demonstrated that the fluorine atoms were participating in the combustion reactivity of this fuel. These results were important in the design of the most appropriate target compounds that would incorporate the desired and necessary combustion properties.

During a visit by Dr. Brel to Dr. Dolbier's lab at the University of Florida, he demonstrated synthesis of a precursor to one of the early synthetic targets investigated in this study. He demonstrated results related to the synthesis of 1,5-derivative, $\text{SF}_5\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CHSF}_5$ and its possible thermal conversion to the 3,4-derivative, via a Cope-rearrangement. Unfortunately, Dr. Brel was not able to get this conversion to occur experimentally. This result was consistent with earlier DFT calculations performed in this study that indicated a + 5 kcal/mol enthalpy for the desired conversion. These results reveal that the steric size of the SF_5 -substituent outweighs its favorable electronic influence on the rearrangement, and thus prevents its occurrence. Based on these results and keeping in mind the preliminary combustion work of Prof. Slutzky, the choice of targets was modified.

In the meantime, Dr. Brel and Dr. Dolbier met at the Boston ACS meeting in August to discuss Dr. Brel's recent synthetic results that are related to this project. He has continued his efforts and has synthesized a number of novel monomers, in particular 1- SF_5 -1,3-butadiene, an interesting molecule that could well play a role as a polymer precursor at some point in the future, should the current two target compounds give rise to unexpected problems.

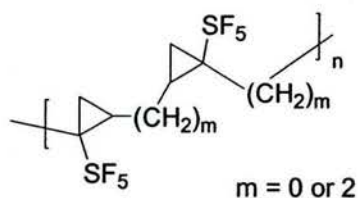
3. Identification of target materials/polymers

In considering possible targets, it was considered desirable to (a) incorporate as high a ratio of SF_5 to carbon as possible, to increase density, increase flash point, and increase the potential for free fluorine during combustion, and to (b) incorporate as much strain as possible, to increase the enthalpy of combustion of the material.

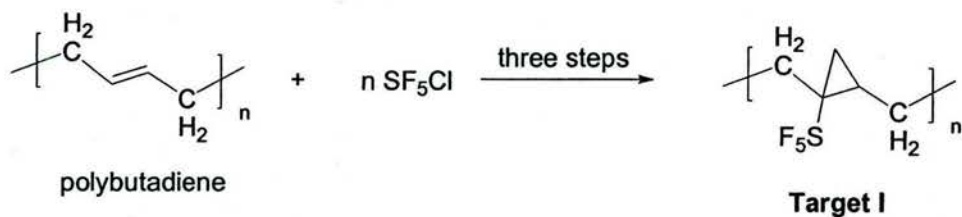
Two such targets were chosen as fulfilling these criteria and also being feasible synthetically, using the new SF_5Cl methodology.

Overall Goal:

Oligomers/Polymers of the type:

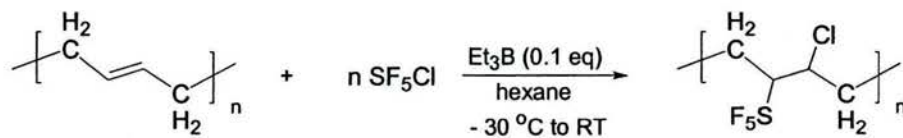


Specific Targets:

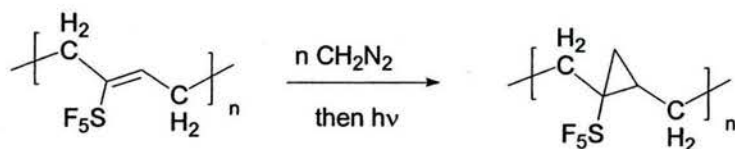
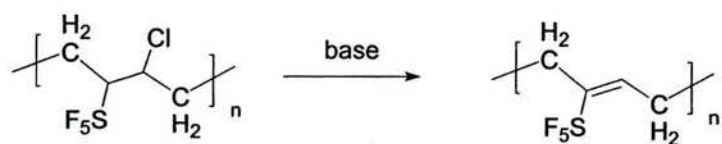


4. Application of new SF₅Cl methodology to the preparation of these target materials

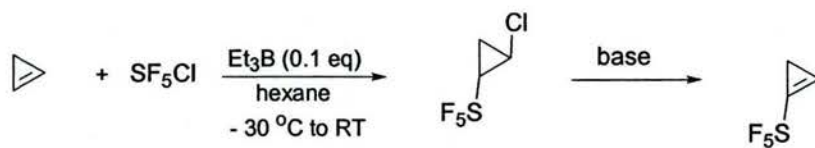
Target I:



polybutadiene



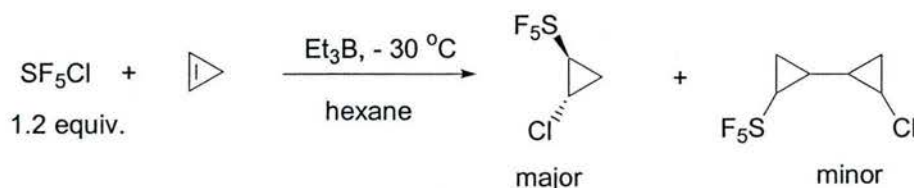
Target II:



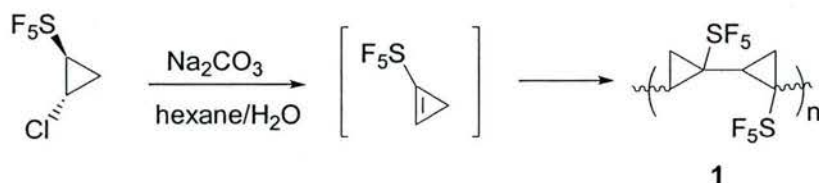
5. Progress toward synthesis of the Targets

Target I: Polybutadiene with perfect structure integrity has been prepared by ADMET polymerization of 1,5-hexadiene, and SF_5Cl has been successfully added to the double bonds of the polybutadiene. The subsequent steps of elimination, diazomethane addition and deazetation to Target I are well precedented.

Target II: Utilizing the new method for introduction of the SF_5 -substituent into aliphatic compounds, the addition of SF_5Cl to cyclopropene was successfully carried out:



By using a 3-fold excess of the SF_5Cl , the desired 1:1 adduct was formed virtually exclusively in almost quantitative yield. Although this reaction was carried out in an open flask at $-78\text{ }^\circ\text{C}$, it would be better run, especially in large scale, in an autoclave. Both starting materials are gases, and the reaction is sufficiently exothermic to cause an initial rapid increase in pressure, which sometimes caused problems in the open flask, although experience was gained in how to control and run the reaction safely.



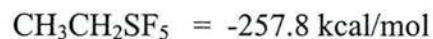
Therefore, utilizing this new method for introduction of the SF_5 -substituent into aliphatic compounds, SF_5Cl was successfully added to cyclopropene, and elimination to

form the unstable 1-pentafluorosulfanylcyclopropene was carried out. Conditions must be established for isolation of this reactive monomer and for its free radical polymerization to give Target II.

Cyclopropene is made in one step from inexpensive allyl chloride, in high yield, and therefore should be an inexpensive starting material. With SF₅Cl commercially available in the United States, and also potentially inexpensive in quantity, target polymer 1 should be relatively inexpensive to prepare in quantity.

6. Computational Efforts

Using B3LYP/6-31+g(2df,2p)//B3LYP/6-31g(d) methodology in conjunction with the Gaussian 98 computational program, this study utilized isodesmic equations to calculate the heats of formation of a number of model compounds:



The results of these calculations were provided to Len Caveny for more extensive thermochemical calculations.

7. Publications and Presentations

Ait-Mohand, Samia and William R. Dolbier, Jr., "New and Convenient Method for Incorporation of Pentafluorosulfanyl (SF₅) Substituents into Aliphatic Organic Compounds", *Organic Letters*, 4, 17, 2002, pp. 3013-3015

CONCLUSIONS

Based on the results of this Phase I study, two high density, pentafluorosulfanyl (SF₅) group-containing polymers have been identified as feasible products. Important properties that should be characteristic of these two products are that (a) they will be high

melting solids, (b) they will have high thermal stability ($>350\text{ }^{\circ}\text{C}$), and (c) they will have excellent air and moisture stability. Therefore, they will have a long shelf life. Further, it is expected that these materials may be able to be used as matrix materials in mixtures with certain, *true* high-energy materials such as $\text{NF}_4^+\text{BF}_4^-$ or even N_2F_4 .

A new, broadly significant synthetic methodology for introduction of the SF_5 -substituent into aliphatic compounds has been invented that can be applied to the preparation of either of these two designated target products. Preliminary synthetic studies have demonstrated the feasibility of preparation of both of these products and the understanding of the chemistry that has been gained from this work indicates that scale up of the procedures should not pose a special problem. In addition, preliminary indications show that the cost of preparing either of these two products on a large scale should be relatively low.